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Tracing the Efficiency of Secondary Treatment Systems

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Abstract

A technique for mapping the three-dimensional performance of secondary treatment systems is described. [^{14}C] oleic acid was added to samples collected from various locations in the system. Each mixture was placed in a vial capped at both ends with semipermeable membranes, returned to its original position in the pond, and then retrieved after 1 day. The amount of radioactivity remaining after correction for leakage and nonbiological losses is a measure of biological activity. The approach revealed that water-column biodegradation was only one of many pathways for oleic acid removal, with sorption to solids also being important, and, perhaps, dominant. Furthermore, it rationalized performance differences between an AST and an ASB.

Introduction

The performance of secondary treatment systems is typically controlled by adjusting parameters such as the aeration level, biomass population, and nutrient load. The approach is relatively straightforward for small activated sludge systems approximating CSTR behavior. Large aerated stabilization basins (ASBs) are much more difficult to optimize on account of their inherent inhomogeneity. It is difficult to evaluate BOD removal at a particular location in an ASB, since mixing tends to even out DO and BOD. Furthermore, the contribution of water-column biodegradation vis-à-vis chemical reaction or settling cannot be easily deter-

mined. In this paper, we illustrate a new chemical-specific technique for mapping pond efficiency at different locations and depths, demonstrate its utility in tracing BOD removal efficiency along an ASB, and use it to compare the behavior of ASBs and activated sludge systems (ASTs) with respect to oleic acid, a model pulp mill effluent component.

Approach

The approach was initially developed to evaluate the biodegradation of organochlorine compounds produced during pulp beaching (1). Briefly, a pond sample is taken from a given depth and location and spiked with a radioactive analog of the test compound. [^{14}C] oleic acid (OA) was used in our application as a marker for BOD; fatty and resin acids are particularly relevant in pulp mill effluents since some of them have been linked to aquatic toxicity (2-5). The amended sample is placed in a vial capped at both ends with semipermeable membranes, and the vial is returned to the original location of the sample in the pond. The membranes partially restrict leakage of OA, but allow relatively free flow of oxygen and nutrients. The vial is retrieved after a day, and the amount of OA remaining (after correction for leakage and nonbiological losses) is used to measure biological activity at that location. While OA is only one of a number of long chain acids released from pulping operations, any compound that measurably biodegrades and whose leakage from the vial is significantly retarded by the membrane can be used.

Semipermeable membrane samplers have been used extensively for passive environmental monitoring of both surface and groundwater (6,7), and a recent report describes an extension to screening microorganisms for their ability to degrade groundwater contaminants (8). The novelty of our application lies in its use of membranes for studying in-situ treatability. Recognizing that ASBs are too heterogeneous and site-specific to be adequately reproduced in the laboratory, we elected to run controlled experiments in the field. A drawback of our methodology is that a single compound, OA in this case, surrogates for all influent BOD. While the results are valid for comparing the relative performance at different locations in the pond, the absolute efficiencies are likely to be biased. This same attribute is also

a strength; the in-situ treatability of specific chemicals large enough to be retained in the vial can be directly determined across the pond.

Our specific objectives were to: (i) track pond efficiency across the lagoon, (ii) determine how much OA was removed through water-column biodegradation, (iii) evaluate oxygen utilization, (iv) assess the depth dependence of biodegradation, and (v) compare ASB performance with that of an activated sludge treatment (AST) system. Samplers were usually installed in pairs. For ASBs, one was tied to the support of the floating aerator so as to be within the aerator throw; the other was placed in a more quiescent region outside the aeration circle. The difference in OA reactivity between the pair provided a comparative measure of oxygen utilization. Measurement of biodegradation rates across the pond allowed the pond efficiency to be progressively traced.

As detailed earlier (1), the membrane holds the microorganisms captive in the vial, but permits partial leakage of the substrate. Ideally, all the substrate would be restricted to the vial, but a membrane of pore size small enough to achieve this would also restrict flow of inorganic ions. We compromised on a membrane that allowed flow of nutrients and dissolved oxygen (DO), but which only partially restricted the leakage of radioactive substrate. A PVC sampler with holes drilled at 1-foot depth intervals accommodated the vials. Five closely-spaced holes were drilled at 2-inch intervals at about 9 feet for measurement of precision. In order to account for nonbiological losses through leakage, sorption, and chemical degradation, formalin was added to vials at every other depth location to sterilize their contents. Now, the difference in residual substrate between "live" and sterile vials at adjacent depth intervals was a measure of water-column biodegradation.

Leakage of the radiolabeled substrate is not necessarily uniform along the vials in a sampler, since, for example, the membrane surface in a given vial may be partially clogged by lagoon particulates. These differences were accounted for by adding $^{36}Cl^-$ to the solution as a conservative tracer. Since loss of $^{36}Cl^-$ should only occur through diffusion, its rate of removal was used to normalize the rate of [^{14}C]OA diffusion from the same vial. Since the diffusion of both [^{14}C]OA and $^{36}Cl^-$ followed first-order kinetics, the [^{14}C]OA lost through biodegradation could be obtained as follows.

The ratio of first-order rate constants for diffusional loss of OA (k_{OA}) and $^{36}Cl^-$ ($k_{chloride}$) from a sterilized vial is

$$\frac{k_{OA}}{k_{chloride}} = \frac{\ln[OA]_o - \ln[OA]}{\ln[chloride]_o - \ln[chloride]} \quad (1)$$

Since live and sterile vials were (usually) alternated, this ratio was averaged for a pair of sterile vials straddling a "live" vial to give $(k_{OA}/k_{chloride})_{sterile}$. Assuming that the same $k_{OA}/k_{chloride}$ ratio for diffusional loss applies to both live and sterilized vials, then the diffusional OA loss from a live vial can be obtained from the equation

$$(k_{OA})_{live} = (k_{OA}/k_{chloride})_{sterile}\,(k_{chloride})_{live} \quad (2)$$

This procedure normalizes small differences in OA diffusivity caused by variations in membrane permeability. The OA remaining in the live vial after diffusion ($[OA]_{post\text{-}diff}$) is

$$[OA]_{post\text{-}diff} = [OA]_o \exp\{-(k_{OA})_{diff}\, t\} \quad (3)$$

Substituting from Eq. (2),

$$[OA]_{post\text{-}diff} = [OA]_o \exp\{-(k_{OA}/k_{chloride})_{sterile}\,(k_{chloride})_{live}\, t\} \quad (4)$$

$$= [OA]_o \exp\{-(k_{OA}/k_{chloride})_{sterile}\, \ln[chloride]_o/[chloride]_{live}\} \quad (5)$$

Hence, the amount of OA biodegraded is

$$[OA]_{bio} = [OA]_{post\text{-}diff} - [OA] \quad (6)$$

where [OA] is the concentration remaining in the live vial at the end of the trial. After one day of exposure, the diffusional loss of OA exceeded the amount removed through biodegradation.

In summary, the approach comprises the following steps.

1. Samples are drawn from various depths at a given location in the lagoon. Each sample is amended with a solution containing [^{14}C]OA and $^{36}Cl^-$.
2. The amended samples are placed in vials capped on both ends with semipermeable membranes. The membranes permit flow of oxygen and nutrients, hold the organisms in place, and partially restrict outflow of OA.
3. The vials are placed in samplers at 1-foot intervals extending to the bottom of the lagoon. Vials at alternate depth locations are sterilized, and are retrieved after 1 day.
4. The OA and $^{36}Cl^-$ are determined in each vial. In order to minimize variations in diffusivity for membranes attached to the various vials in a sampler, the [^{14}C]OA in each vial is normalized with respect to the $^{36}Cl^-$ remaining in that vial. Comparison of the OA in a live vial to that in adjacent sterilized vials provides the amount of biodegraded OA.

We implicitly assume the initial step to be rate-limiting, since we cannot detect situations where an oleic acid molecule fragments into smaller pieces that may then diffuse out. Thus, the method principally measures relative biodegradation at various locations.

Description of the field sites

Field work was done at Georgia-Pacific mills at Brunswick, GA, and at New Augusta, MS (known in the industry as the Leaf River mill). The Brunswick mill pulps both hardwood and softwood in 19 digesters, 8 for hardwood and 11 for pine. Three ClO_2 bleach lines are run; two process pine, and one swings between hardwood and pine. Total production was about 2150 tons/day. A primary clarifier with a holding capacity of 12.3 million gallons was operated at a rate of 20-24 million gallons/day. Secondary treatment occurred in a 12-acre presettling basin, a 137-acre aerated lagoon, and a 6-acre settling lagoon, for a total nominal retention of 5 days. The lagoon currently has 61 surface aerators, and total flow to the river was about 35 mgd at the time of the study. A schematic of the ASB is shown in Figure 1.

During the study, daily production at Leaf River, which pulps both hardwood and softwood, approximated 1500 tons of bleached Kraft market pulp. A single five-stage D-(Eop)(D)(Ep)(D) bleach line alternated between hardwood and softwood. The treatment system consisted of a bar screen, two primary clarifiers with each providing a 4-hour detention, equalization, cooling, activated sludge treatment in an aeration basin, two secondary clarifiers, and a final holding pond. The equalization basin, with 10 floating aerators, had a detention time of 16.5 hours. The wastewater then flowed to a cooling tower which discharged to a 48-million gallon aeration basin with a 45-hour detention. The solids retention time was 3.5 days. The flow was divided between two secondary clarifiers, each with a detention time of 9.4 hours. Approximately 8 mgd (40%) of the secondary sludge was recycled to the aeration basin. The secondary clarifiers led to a holding pond (with a detention time of 3 to 12 days), which discharged continuously through diffusers to the Leaf River. Total flow to the river was about 18 mgd.

Experimental

[^{14}C]OA, both uniformly labeled and labeled only at the carboxylic acid group, was obtained from New England Nuclear, as was [^{36}Cl]HCl. Samples (20 mL) taken from specific depths and locations were amended with about 20,000 dpm of the [^{14}C] and 70,000 dpm of the [^{36}Cl] materials and placed in the membrane-capped vials. Each sampler held vials at 1-foot depth intervals; precision was measured at five closely spaced vials at about 9 feet. Vials at every second depth interval were sterilized with 1.5 mL of 40% (v/v) formalin, and the sampler was positioned in the treatment system. Vials were occasionally lost from samplers adjacent to the aerators due to turbulence. The "live" vials were preserved with formalin after retrieval, and the residual radioactivity in each vial determined by liquid scintillation counting. The vials were retrieved after only 1 day even though the HRT of the systems were much longer because OA diffused quite rapidly. More than half of the initial OA was lost from the sterilized vials, and a longer exposure would have minimized differences between the live and sterilized vials. Kinetic studies were conducted by placing several samplers at a single location each at Brunswick and Leaf River. A sampler was withdrawn periodically, and

the results from the several live vials contained therein were averaged. Further details are provided in references 9 and 10.

Results and Discussion

Studies at the Brunswick ASB

Field studies were conducted at Brunswick with OA labeled only at the carboxylate group (September 1995) and with uniformly labeled material (May 1996). A typical profile with the former is illustrated in Figure 2, and shows no depth dependence. Hence, results from all the vials in a sampler were averaged, and these are reported in Table 1. The precision values in Table 1 were calculated from the ^{14}C recovered from the five closely spaced vials in each sampler. Note that the difference between aerated and nonaerated samples is significant only at location 14, which is at the top edge of the pond. Lithium tracer work (11) suggests holdup in this region of the pond, and it is possible that the difference in reactivity is caused by reduced mixing. The relatively stagnant conditions will favor DO buildup within the throw of aerator 14. This is consistent with the relatively high degradation efficiency (40%) at this location. The nonaerated sample was taken near the bank where mixing would be uneven. Hence, the difference in DO between the aerated and nonaerated zones could be appreciable, leading to a difference in biodegradation. In other words, the enhanced reactivity in the aerated region comes at the expense of reduced reactivity in the nonaerated zone.

Corresponding data with uniformly labeled OA are included in Table 1, with a typical profile illustrated in Figure 3. The aerated zones are more active in all cases, suggesting that the injected air is preferentially utilized near the aerators before mixing is complete. Biological activity diminishes rapidly after aerator 17, and there is little activity beyond location 56. Data from the uniformly labeled and carboxylate-only labeled material contrast in that biodegradation of the former progressively decreases along the pond. This suggests that while decarboxylation occurs rapidly, further degradation is slower. As noted earlier (5), OA sorbs rapidly to biomass, and it is possible that its bioavailability may decrease with time. If so, then the degradation of the alkyl groups would be retarded relative to that of carboxylate.

Studies at the Leaf River AST

Samplers were placed at two locations, arbitrarily labeled A and B, in the AST during September 1995. Fewer sampling points were necessary, as compared to the Brunswick ASB, since the Leaf River system was well mixed. Results from location A are illustrated in Figure 4, and the results are summarized in Table 2.

Kinetic studies

Kinetics were attempted at aerator 25 at Brunswick and at location A at Leaf River. Biodegradation at various time intervals is plotted in Figure 5. Neither the Brunswick nor the Leaf River plot follows first-order kinetics, with the Leaf River data diverging more sharply. We attribute the deviations to sorption to biomass or other particulates, which competes with biodegradation and reduces substrate bioavailability. Liu et al. (5) recently demonstrated that resin acids sorb rapidly to sludge. Since ASTs have higher solids levels than do ASBs, the degree of sorption should be higher at Leaf River, as observed. These results indicate that even though fatty acids are largely removed during secondary treatment (12), water column biodegradation is unlikely to be the only pathway. Since OA is of low water solubility, it will tend to sorb strongly to particulates, and it is reasonable for sorption and settling to be partially responsible for its removal from the water column. We emphasize that our conclusions only apply to the water column and do not address the fate of OA in the sludge bed. Certainly, benthal layer biodegradation, or benthal feedback and subsequent water-column degradation are also possible.

Both Brunswick and Leaf River report more than 95% BOD reduction across their treatment systems, and the Figure 5 data indicate a much lower reduction of OA over the hydraulic retention time. The BOD result is expected to differ from that of OA for several reasons. First, OA is only one component of BOD, and lighter components should degrade faster in the pond. Second, the pond undergoes spray aeration, and oxygen transfer to the airborne droplets is much efficient than to our samples, which are held captive in the samplers. Third, OA is partially removed from the water column through sorption to MLSS, which would settle out and constitute a removal mechanism. In our experiments, they

would remain in the vial and be counted along with the dissolved material. These differences must partially account for the higher BOD removal realized in the field.

A recent laboratory study (5) showed that a substantial fraction of a suite of resin and fatty acids (which included OA) sorbed to MLSS in about 30 minutes. Biodegradation occurred over 12 hours, which suggests that the sorbed material was bioavailable. On the other hand, our work at both Brunswick and Leaf River indicates that sorbed OA is not bioavailable during the measurement period. The distinction, which could originate from differences in DO, biomass age, etc., points to the real utility of our field approach. While the interior of the vial does not exactly duplicate the environment outside, it is a much closer approximation than a laboratory simulation. Laboratory results may not necessarily extend to the field, especially where multiple degradative pathways are possible.

Conclusions

We have demonstrated a new method that allows the performance of a treatment system to be mapped in three dimensions through use of a labeled model compound. We have shown that differences in treatability at different locations in an ASB can be detected despite mixing. The method allows the fate and distribution of a selected effluent component to be determined. In our case, water-column biodegradation of oleic acid is just one removal mechanism, and possibly a minor one. The long-term value of the approach is that it provides a microscale understanding of secondary treatment. An immediate practical outcome is that the least efficient aerators can be identified and shut off during periods of peak electrical demand when the cost of power is the highest. This was done at Brunswick, where substantial savings are being realized (11).

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Table 1: Water column OA biodegradation at Brunswick				
location	**percent OA biodeg ± σ (n)**		**precision (%)[1]**	
	aerated	**nonaerated**	**aerated**	**nonaerated**
carboxylate labeled OA				
14	40 ± 10 (8)	10 ± 3 (4)	10	5
9	23 ± 4 (11)	18 ± 3 (3)	3	4
62	28 ± 9 (4)	30 ± 10 (3)		
uniformly labeled OA				
34	32 ± 3 (7)	26 ± 2 (7)		
17	11 ± 1 (12)	7 ± 2 (9)		
56	13 ± 2 (7)	11 ± 1 (7)		
31	5 ± 2 (8)	1.0 ± 0.4 (4)	4	
3	9 ± 9 (9)	3 ± 1(4)	14	
[1]standard deviation of [^{14}C] recovered from five closely spaced samples at about 9 feet.				

Table 2: Water-column OA biodegradation at Leaf River		
zone	percent biodegra-dation (σ)	n
Leaf River (A)	25 (2)	9
Leaf River (B)	30 (4)	10

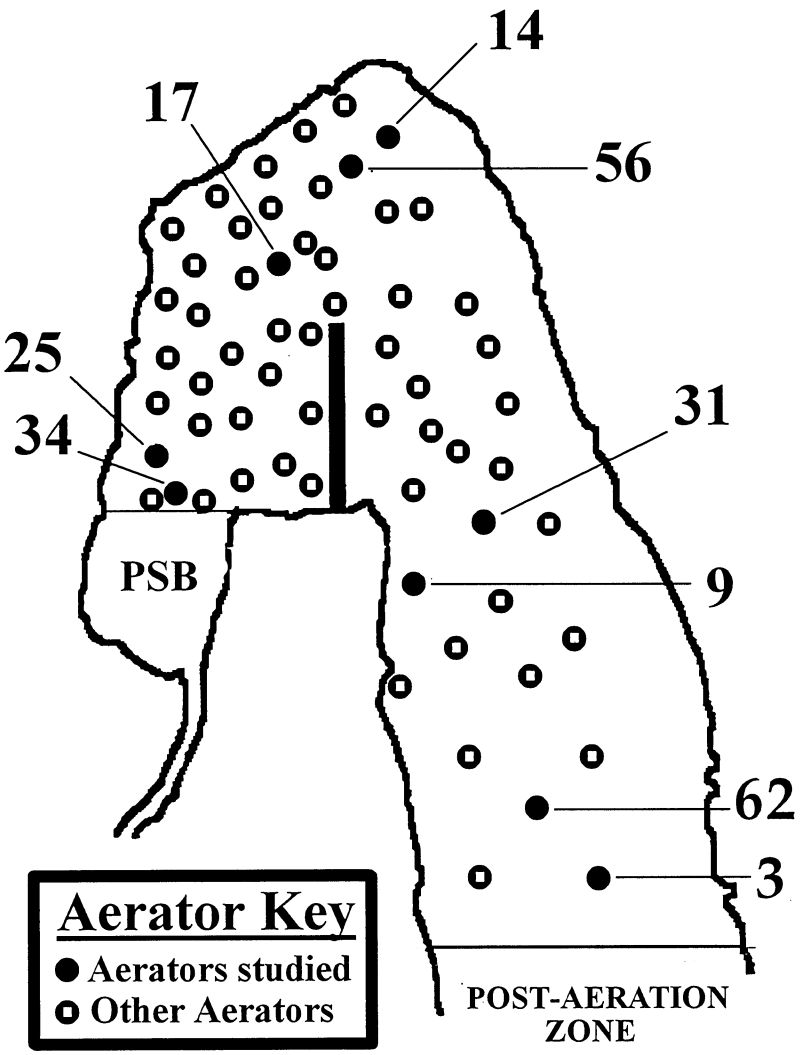

Figure 1: Schematic of the secondary treatment system at Brunswick.

(PSB refers to the presettling basin)

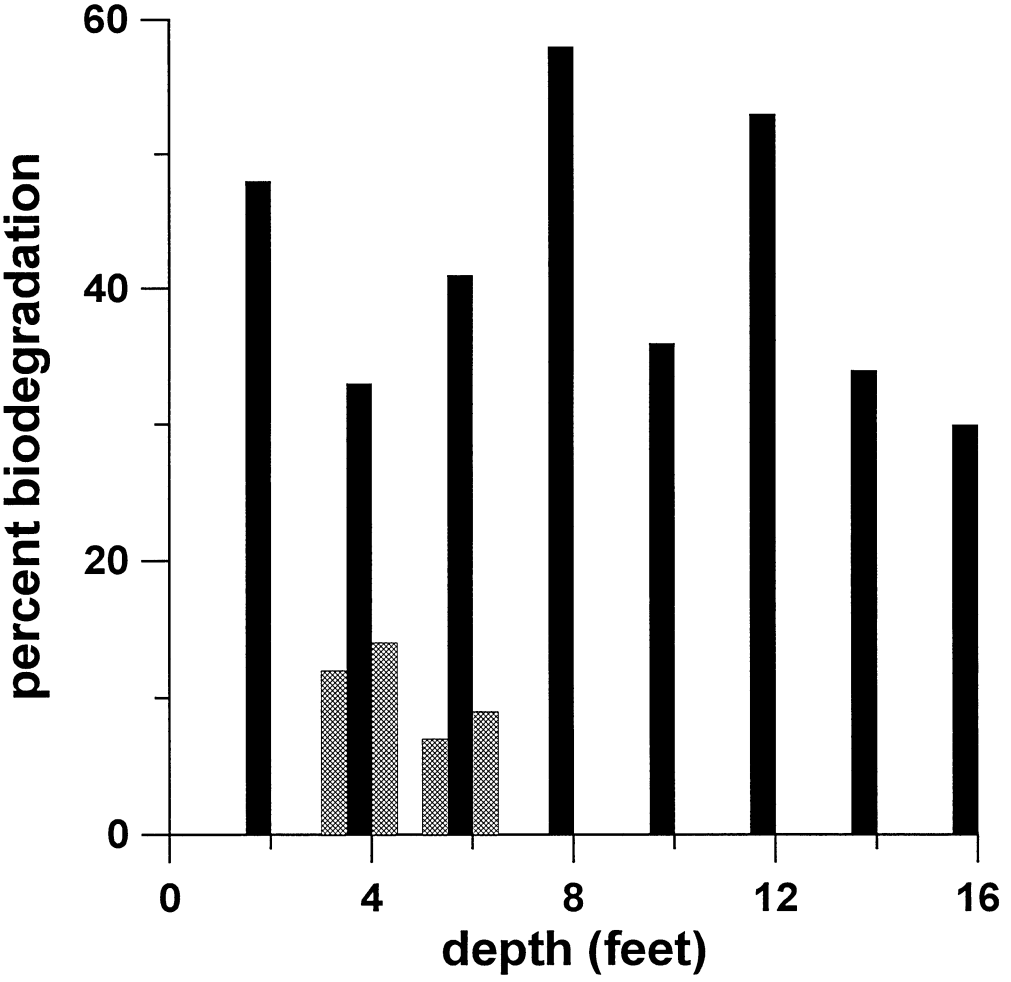

Figure 2: Biodegradation of OA at aerator 14 (dark: aerated; hatched: nonaerated).

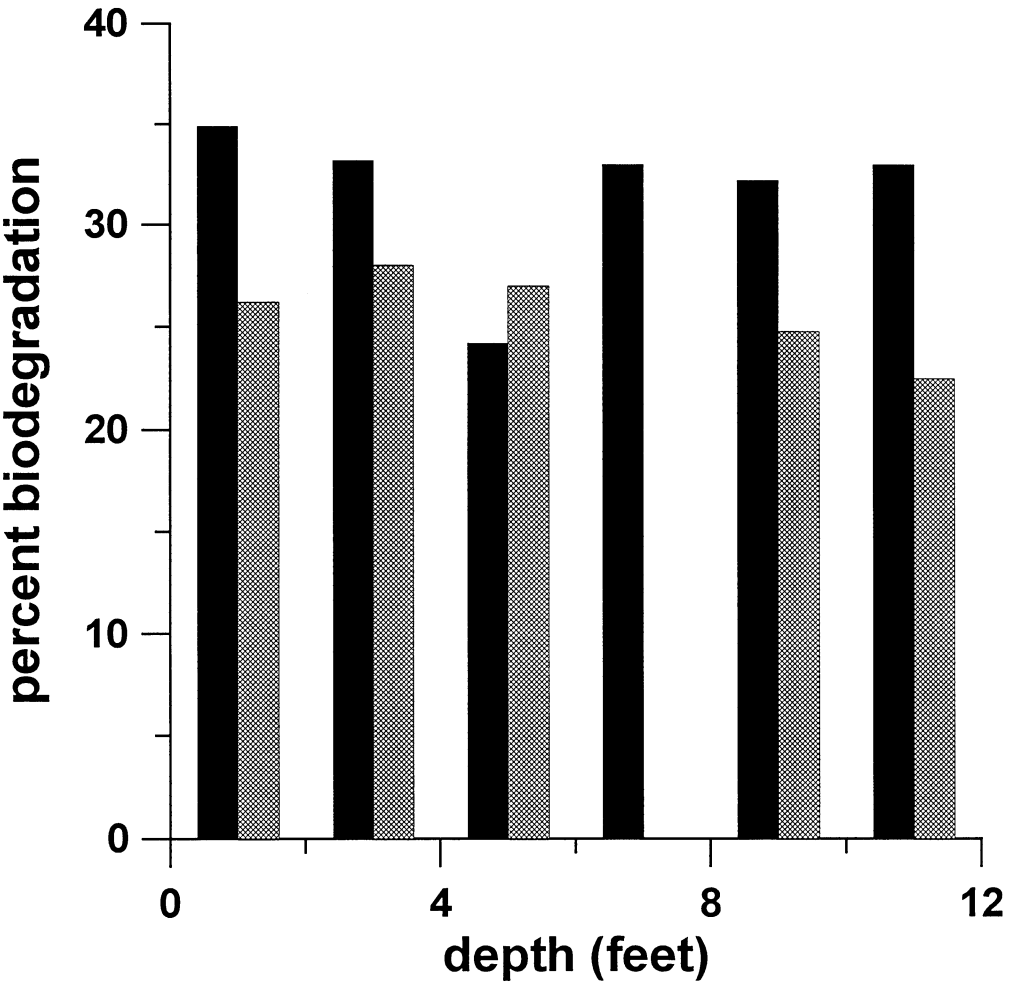

Figure 3: Biodegradation of OA at aerator 34 (dark: aerated; hatched: nonaerated).

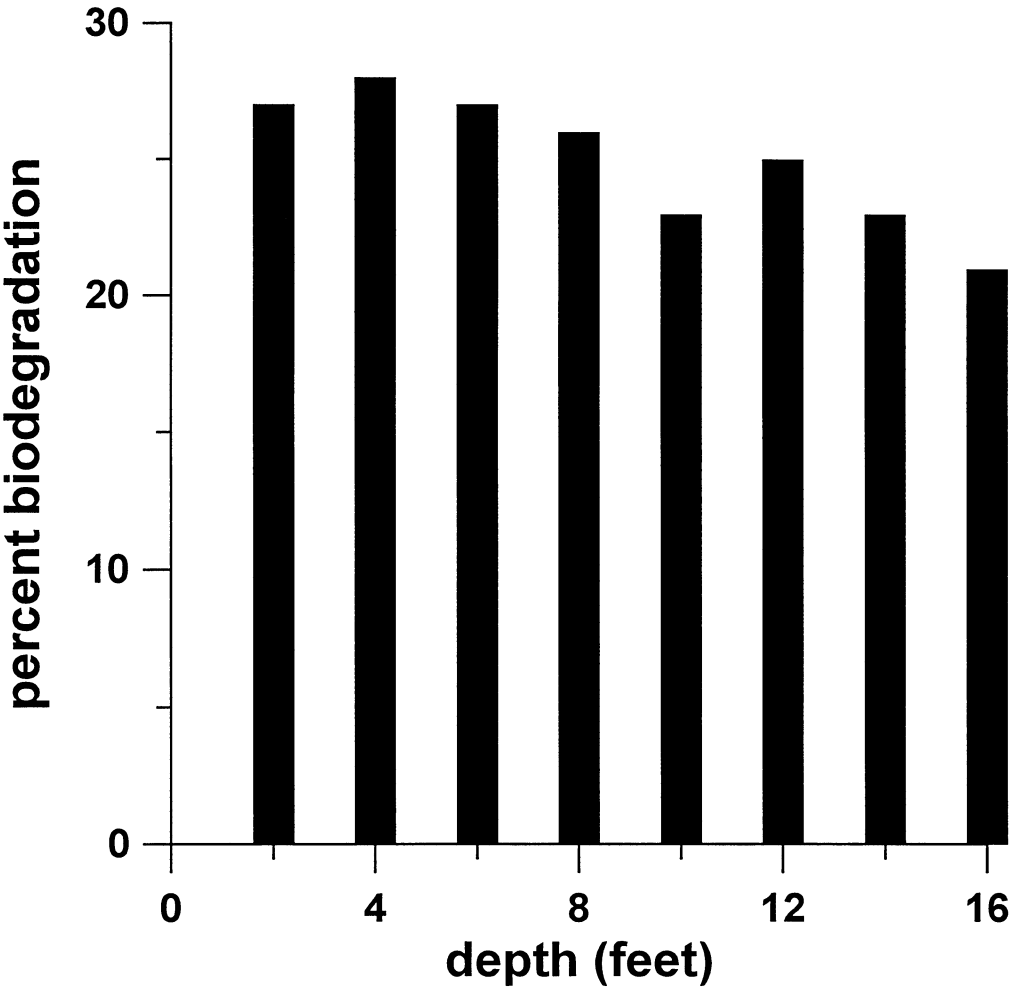

Figure 4: Biodegradation of OA at location A at Leaf River.

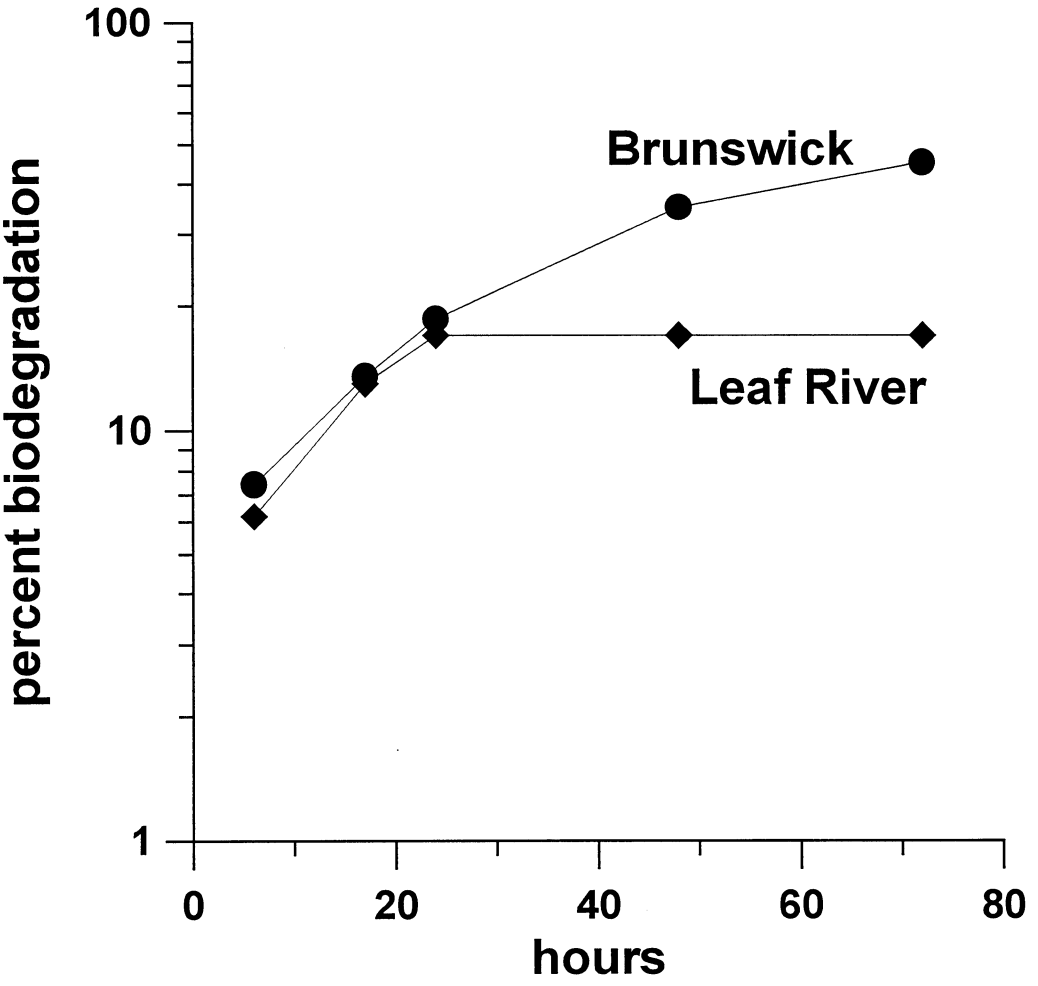

Figure 5: Rates of OA biodegradation